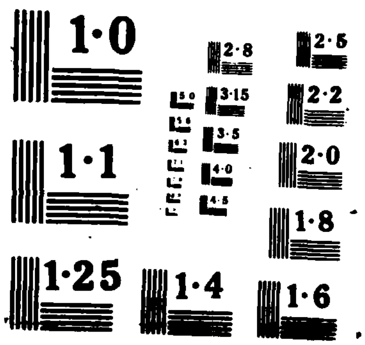
AD-A176 113 PHOTOSTABILITY OF DYES USED FOR SPRAYED CHEMICAL AGENT SIMULANTS(U) CHEMICAL RESEARCH DEVELOPMENT AND ENGINEERING CENTER ABERDEEN.. J H KELLER ET AL. DEC 86 1/1

UNCLASSIFIED CRDEC-TR-87018 F/G 15/2 NL


1·0
2·8
2·5
3·15
2·2
3·5
1·1
2·0
4·0
1·8
1·25
1·4
1·6

(9)

CHEMICAL
RESEARCH,
DEVELOPMENT &
ENGINEERING
CENTER

CRDEC-TR-87018

AD-A176 113

PHOTOSTABILITY OF DYES USED FOR SPRAYED CHEMICAL AGENT SIMULANTS

by Jennifer H. Keller
Albert Deiner
MUNITIONS DIRECTORATE

December 1986

U.S. ARMY
ARMAMENT
MUNITIONS
CHEMICAL COMMAND

Aberdeen Proving Ground, Maryland 21010-5423

Disclaimer

Distribution Statement

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) CRDEC-TR-87018	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION CRDEC	6b OFFICE SYMBOL (If applicable) SMCCR-MUC
7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) Aberdeen Proving Ground, MD 21010-5423	7b. ADDRESS (City, State, and ZIP Code)
8a. NAME OF FUNDING/SPONSORING ORGANIZATION CRDEC	8b. OFFICE SYMBOL (If applicable) SMCCR-MUC
9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) Aberdeen Proving Ground, MD 21010-5423	10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO
	1L162706	A553-J	

11 TITLE (Include Security Classification)

Photostability of Dyes Used for Sprayed Chemical Agent Simulants

12 PERSONAL AUTHOR(S)
Keller, Jennifer H., and Deiner, Albert

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM 83 Aug TO 83 Dec	1986 December	23

16 SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP
15	02	

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

FD&C red #3, FD&C yellow #6, Photodecomposition, Rhodamine B, FD&C blue #1, Photostability, FD&C green #3, Basic fuchsin (continued on reverse)

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Polyethylene glycol 200 and water mixtures are used as training aids for field exercises. To train troops in accepted methods of decontamination, simulated aerial spray per unit area is determined by collecting in a sampling pan the aerial spray of a known area and washing the collected material with a known volume of water. The intensity of absorption of the collected material, measured photometrically, is related to a mass of dyed aerial spray. If the dye is sensitive to sunlight, fading or photodecomposition occurs and leads to erroneous measurement of the mass of aerial spray collected. This investigation studied various potential dyes for their photostability and their potential use as color for aerial spray simulants.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED
22a NAME OF RESPONSIBLE INDIVIDUAL TIMOTHY E. HAMPTON	22b TELEPHONE (Include Area Code) (301) 671-2914 — 22c. OFFICE SYMBOL SMCCR-SPS-T

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

18. SUBJECT TERMS (cont)

Solar simulator
Dye tracer
Dye spectrum
Photodecomposition kinetics
Polyethylene glycol 200 mixtures
Irradiance

PREFACE

The work described in this report was authorized under Project No. 1L162706A553-J, Chemical Training and Trailing Agents and Equipment. This work was started in August 1983 and completed in December 1983. The experimental data are recorded in laboratory notebooks 82-0160 and 83-0164.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

Acknowledgments

The authors acknowledge Phyllis M. Christy for typing and assembling the draft of this publication and Grace E. O'Connor for preparing the camera-ready manuscript.

Blank

CONTENTS

LIST OF FIGURES

PHOTOSTABILITY OF DYES USED FOR SPRAYED CHEMICAL AGENT SIMULANTS

1. INTRODUCTION

Training U.S. Army forces in defensive measures during chemical attack is a requirement of high importance and impacts on the defensive posture of the armed forces of the United States. To meet this requirement, the Munitions Directorate, U.S. Army Chemical Research, Development and Engineering Center, developed various training aids for use in the field. These training aids mimic actual chemical warfare agents and weapons and serve to indoctrinate troops in the use of protective equipment during mock attack. One of the training aids under investigation is a simulant aerial spray that has properties similar to the persistent nerve agent VX.

The Surgeon General of the U.S. Army placed restrictions on the use of toxic simulants as training aids. Guidelines state that training aid simulants must be nontoxic or have extremely low toxicity. We determined that the polyethylene glycols (PEG) are aptly suited for these purposes. These materials are water soluble, approved for human consumption, and are almost innocuous. PEG may be diluted with water to obtain liquids with viscosities and densities similar to VX.

To test the dissemination efficiency of PEG solutions and obtain area coverage and concentration profiles of sprayed PEG solutions, droplets of sprayed PEG must be collected in a pan sampler having a known area. Analysis of the weight of PEG collected in the pan and subsequent reduction of the data to a contamination density (mg/m^2) value is required. A grid of pans laid across the field where the aerial spraying occurs allows you to ascertain the contamination density profile of the disseminated PEG. The formulation of contour lines of equal contamination densities, and subsequent integration over the area subtended, determines the area coverage and dissemination efficiency.

An analysis of the collected PEG in each sampling pan is required. The sampling pan is rinsed with distilled water and the washings collected. Usually 100 cm^3 of water is required for this operation.

The analysis of PEG in aqueous solution is a difficult task. PEG is thermally unstable at its high boiling point. Gas-liquid chromatography can be performed on the neat chemical, but serious difficulties are encountered in determining small quantities of neat chemical agent in the presence of large quantities of water. High-pressure liquid chromatography is an attractive alternative for thermally labile materials. PEG, however, does not have any appreciable absorption bands in the 200- to 700-nm region of the spectrum. This precludes the use of photometric detection. Detection by refractive index is possible but the possibilities of foreign chemicals being collected along with the PEG in field samples cannot be neglected. Another problem in using a colorless liquid as a spray simulant is in the determination of the particle size of the spray. PEG and water mixtures do not cause color changes on the M detector paper, and the measurement of spot size is very difficult or impossible.

Historically, spray tests have been conducted using liquids that were dyed. The spray liquid generally contained 0.1 to 1% dye which served as a tracer for the disseminated material. By using photometric analysis one could easily determine the mass of PEG and water droplets collected in sampling pans. By placing white absorbant cards in a grid on the field, the droplets stained the card and indicate their presence. The measurement of diameter of the drops of known particle size on the card ("spread factor") allowed one to determine the size distribution of the aerial spray. The colored droplets also allowed the military personnel engaged in the training exercise to recognize when they were contaminated by the simulant and to perform the decontamination exercises as required.

Many dyes have been employed as tracers in aerial sprays in previous years. However, given the current guidelines furnished by The Surgeon General in regard to toxicity and safety to troops in the field, these materials can no longer be used. Many of these dyes are toxic, mutagenic, or carcinogenic; and military personnel cannot be exposed to these chemicals.

Since field testing is conducted in sunlit areas, the problem of dye fading or decomposition is of prime importance. Fading or photodecomposition of the dye yields low values in mass recovery of PEG and results in erroneous low values in dissemination efficiency during field testing. The fading or photodecomposition of dyes is a factor that must be addressed in the development of field simulants. The purpose of this report is to document studies with dyes suitable to act as tracers with PEG and water simulants. These dyes were investigated in regard to their intensity of absorption in the visible region of the spectrum (400-750 nm) and their light fastness or resistance to photodecomposition.

2. MATERIALS AND EQUIPMENT

2.1 Materials.[1]

Figure 1 shows the chemical structures of the dye tracers employed in the experiment. The following dyes were used in this study:

- FD&C Green #3. This dye was purchased from Warner Jenkinson (catalog number 6503, lot AB-9086, 89% pure dye), Color Index #42053.

- FD&C Yellow #6. This dye was purchased from Warner Jenkinson (catalog number 8006, lot AB-8737, 89% pure dye), Color Index #15985.

- FD&C Blue #1. This chemical was purchased from Stange Food Color (catalog number 9901, lot AB-3663, 94% pure dye) Color Index #42090.

- Fuchsin, Basic. This compound was purchased from Fisher Scientific (lot 762485) Color Index #42510.

[1]Colour Index, Third Edition, Volume 4, pp 4383, 4087, 4385, 4389, and 4228, The Societty of Dyers and Colourists, Yorkshire, BD12JB, England (1971).

● FD&C Red #3. This dye was purchased from Warner Jenkinson (catalog number 7003, 97% pure dye), Color Index #45430.

● Rhodamine B Extra S. This dye was purchased from General Dyestuff Corp (S.O. 5608), Color Index #45170.

● Solvent. The solvent used was polyethylene glycol 200 (PEG 200).

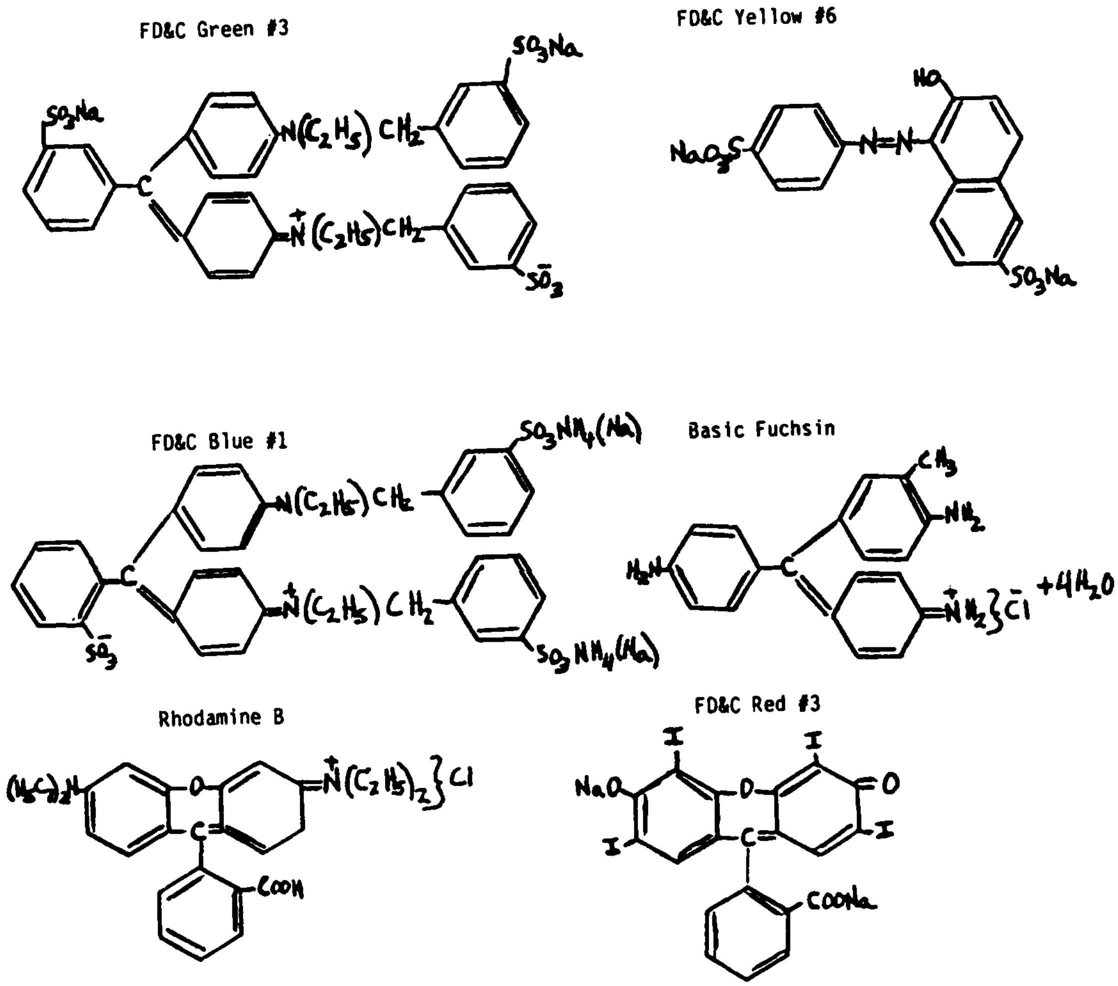


Figure 1. Chemical Structures of Dye Tracers

2.2 Equipment.

The following items were used in this study:

- Beckman Multispectrum Recording Spectrophotometer, Model 5240.
- Turner Spectrophotometer, Model 380.
- Oriel Solar Simulator, Model 81100, equipped with a 300-watt Xenon Lamp Source and an Air Mass 2 filter.
- Oriel Solar Simulator Radiometer, Model 81020.

3. EXPERIMENTAL

3.1 Photodecomposition of Dyes.

Dyes photodecompose by a series of complex reactions. Photodecomposition is initiated by the absorption of radiant electromagnetic energy of a defined frequency corresponding to the absorption spectrum of the dye molecule. Thus, one can define the initiation process by:

$$D + h\nu \rightleftharpoons D^* \tag{1}$$

where,

D is the dye molecule in the lowest electronic state (ground state),

D^* is the first excited electronic state,

h is Planck's constant, and

ν is frequency.

The absorption process is extremely rapid and the lifetime of D^*, generally, is very short. However, D^* can undergo reaction in several ways:

$$D^* \longrightarrow P \tag{2}$$

$$D^* + A \longrightarrow D^*_{red} + A_{ox} \tag{3}$$

$$D^* + B \longrightarrow D^*_{ox} + B_{red} \tag{4}$$

$$D^* + D \longrightarrow D\text{-}D^* \tag{5}$$

One must note that the absorption of light by D to form D* is related to the oxidation potential. It has been shown by quanta mechanical analysis using the highest occupied moleculaı orbital (HOMO) approximations that the electron removed in the oxidation process is the same electron promoted to the first excited electronic state by absorption of photons. Therefore, in many ways D* reacts like D+, the radical cation resulting by electrochemical oxidation.

Equation 2 shows the decomposition of D* to a product P. Generally, the rate of decomposition is slower than the rate of formation of D* and is the rate determining step.

Thus,

$$\frac{dp}{dt} = -k_1 [D^*] \qquad (6)$$

which shows product, P, formation is dependent on D*. This is the general kinetic expression of a first-order reaction.

Similar expressions may be derived for the reactions shown in equations 3 through 5. In each of these examples the concentration of the reactive substrate when in very high concentration does not change appreciably during reaction. The value of $k_2[A]$, $k_2[B]$, or $k_2[D]$ is essentially constant having a value k^1.

Since $k_1 \cdot k^1 = k^3$, the differential equation for these types of reactions reduce to pseudo first-order kinetic expressions.

We have found pseudo first order or first-order kinetics for the photodecomposition of the dyes FD&C Red #3 and Rhodamine B. No attempt was made at product analysis but the adherence to first-order kinetics is entirely consistent to the photodecomposition of dyes. With the dyes FD&C Green #3, FD&C Yellow #6, FD&C Blue #1, and Basic Fuchsin, the reaction rate is probably very slow; and little, if any, decomposition was observed.

3.2 Preparation of Spectral Characterization Standards.

One gram of dye was dissolved in 100 grams of PEG 200 yielding a solution of 1% dye, w/w, in PEG 200. Subsequent dilutions to the concentration range suitable for spectral characterization were accomplished by standard volumetric techniques using distilled water as the diluent. The dyed PEG 200 and water solutions were scanned in the Beckman Spectrophotometer from 700 to 360 nm at a scan speed of 1/4 nm/sec.

3.3 Preparation of Solar Irradiation Standards.

A sample of 1% dye in PEG 200 solution was weighed into a tared glass petri dish. The sample was spread as thin as possible over the dish and then weighed again to obtain a final weight. The sample was solar irradiated, by means of the solar simulator, for various lengths of time.

3.4 Investigational Procedures.

3.4.1 Analytical Sensitivity.

The sampling procedure used in the field consisted of 6-inch diameter polyethylene pans used to collect falling drops of the PEG 200 and dye solution. The sample was then washed from the pan with 100 ml of solvent. The goal of the field tests was to detect ground deposition densities of at least 100 mg of PEG 200 per square meter. Dyestuff concentrations in PEG 200 were constrained to the range of 0.1 to 1.0% due to solubility reasons, costs, and environmental issues.

For purposes of this study, 1% solutions of dye in PEG 200 were used. The requirements for analytical sensitivity are shown in the following calculations:

a. Sampler Area:

$$\pi d^2/4 = (6 \times 2.54)^2 \pi/4 = 182.4 \text{ cm}^2 \text{ or } 0.01824 \text{ m}^2$$

b. Amount of PEG 200 in a sample pan at a contamination density of 100 mg/m^2:

$$(0.01824 \text{ m}^2)\left(\frac{100 \text{ m}^2}{\text{m}^2}\right) = 1.82 \text{ mg}$$

c. Analytical sensitivity of dye in PEG 200 in 100 ml of solvent:

$$1.82 \text{ mg} = 1824 \ \mu\text{g}/100 \text{ ml solvent} = 18.24 \ \mu\text{g/ml}$$

From these calculations, the goal of this analysis was to detect 18.24 μg/ml of PEG 200.

3.4.2 Dye Stability in Sunlight.

The stability of the dye to irradiation by sunlight was studied using a solar simulator equipped with an Air Mass 2 filter. The incident radiation was measured before each trial with a radiometer. After irradiation, each sample was quantitatively transferred to a 100-ml volumetric flask filled with water. The sample was then analyzed at its respective absorption maximum with the Turner spectrophotometer. Turner spectrophotometer was used because of the rapidity of measurement at a single wavelength.

4. RESULTS AND DISCUSSION

4.1 Analytical Sensitivity of Unirradiated Dye and PEG 200 Mixture.

The electronic spectra of each dyed PEG 200 and water solution is shown in Figures 2-7. From these spectra, the absorption maximums in the visible region were used to construct a calibration curve for each solution. At the maximum, a linear regression least-squares fit of the data was performed to obtain a sensitivity factor. The analytical sensitivity of each dye and PEG 200 solution, as read on a 1-cm path cell, is shown in Table 1. The analytical sensitivity was calculated and it was arbitrarily assumed that an absorbance of 0.05 was a valid reading.

The goal of this study was to detect 18.24 μg/ml of PEG 200 using a 1-cm path cell. All dye tracers in PEG 200 at the 1% level failed to meet this requirement. However, we need not necessarily use a 1% dye level concentration or a 1-cm path cell to act as a tracer for the PEG 200. Using the values of concentration shown in Table 1 at a 1% dye level it can be shown that FD&C Blue #1, FD&C Green #3, and Basic Fuchsin would be satisfactory at either the 2% level or using a 2-cm path cell for measurement would detect the desired 18.2 μg/ml of PEG 200. Employing a 2% level dye and a 5-cm path cell would work adequately for Rhodamine B and FD&C Yellow #6. FD&C Red #3 would be satisfactory at the 1% level with a 5-cm path cell.

4.2 Photodecomposition of Dye Tracers.

Exposure of samples to direct sunlight would not be an accurate means of finding the total irradiance that the sample was exposed to due to clouds, haze, time of day, and other atmospheric disturbances. Therefore, a means was sought that would provide a uniform irradiance which mimicked the solar spectrum. The Oriel Solar Simulator was used for this purpose. Shown in Figure 8 is the unfiltered output from the Oriel Solar Simulator.[2] Shown in Figure 9 is the solar simulator output fitted with an Air Mass 2 filter. Air Mass 2 filters were chosen because they represent the closest approximation to the solar radiation in the region of 300 nm to approximately 2,450 nm impinging at the earth's surface.[3] By far, the region between 300 nm and 500 nm was of greatest interest to us as it represents the wavelengths most likely to cause photodecomposition of dyes.

---

[2] Solar Simulation For Research and Industry. Oriel Corporation. Stamford, CT.

[3] Smithsonian Physical Tables. Smithsonian Miscellaneous Collections. Volume 120. Ninth Revised Edition. p 721. Smithsonian Institution, Washington, DC (1954).

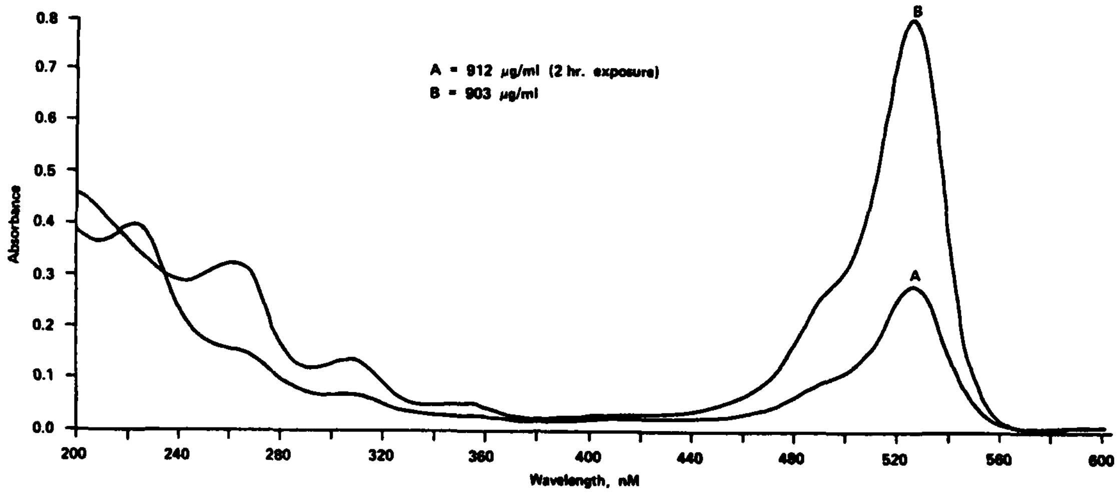


Figure 2. Spectral Characterization of FD&C Red #3

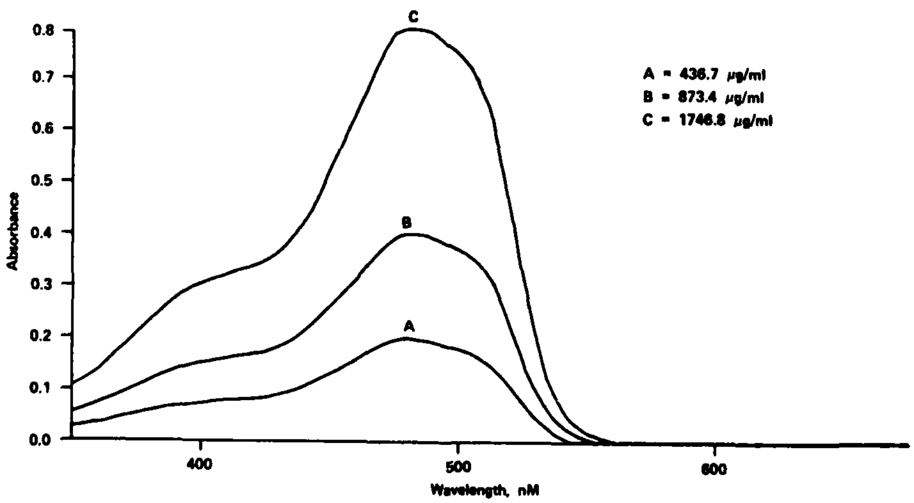


Figure 3. Spectral Characterization of FD&C Yellow #6

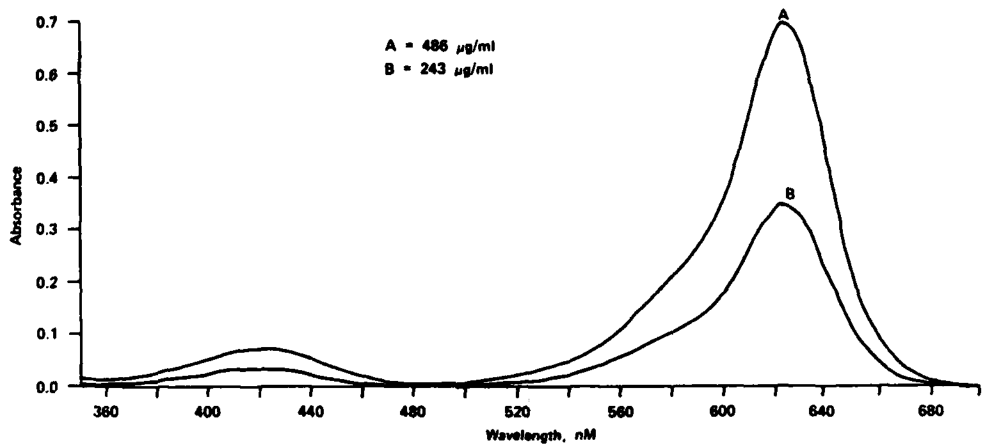


Figure 4. Spectral Characterization of FD&C Green #3

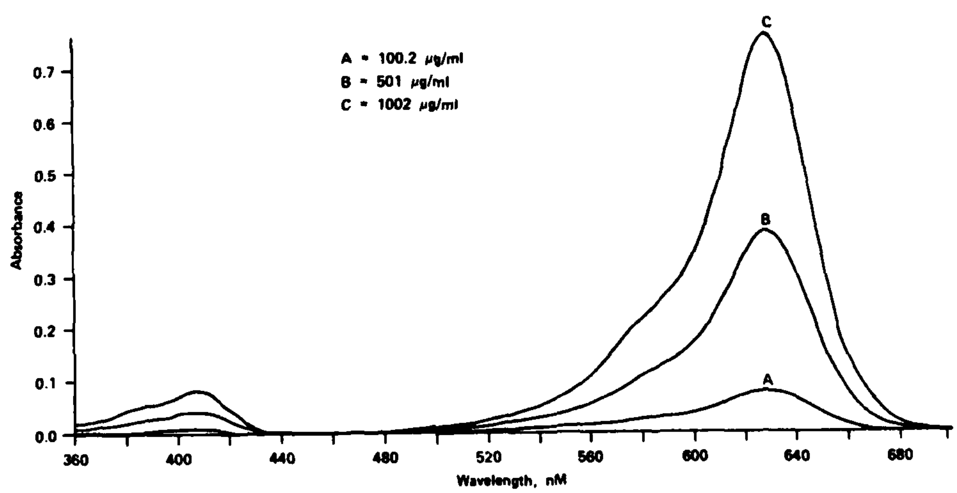


Figure 5. Spectral Characterization of FD&C Blue #1

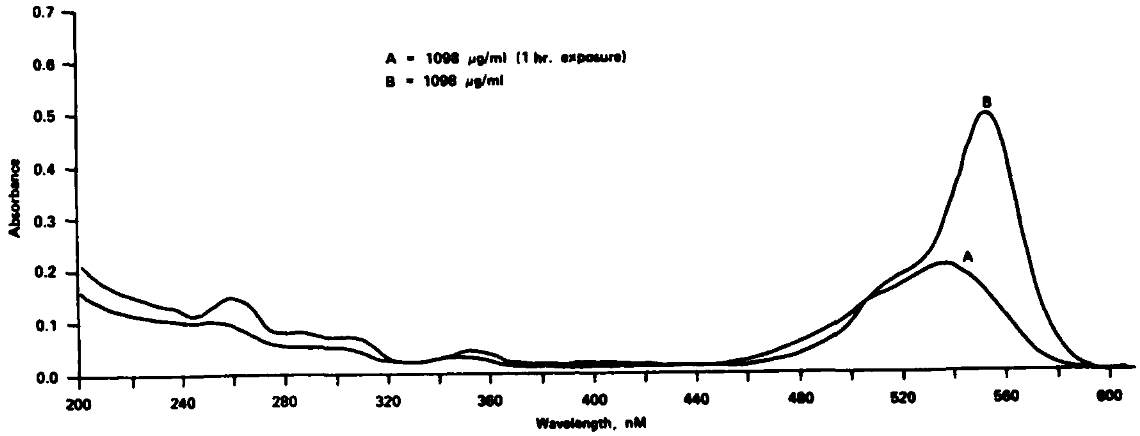


Figure 6. Spectral Characterization of Rhodamine B

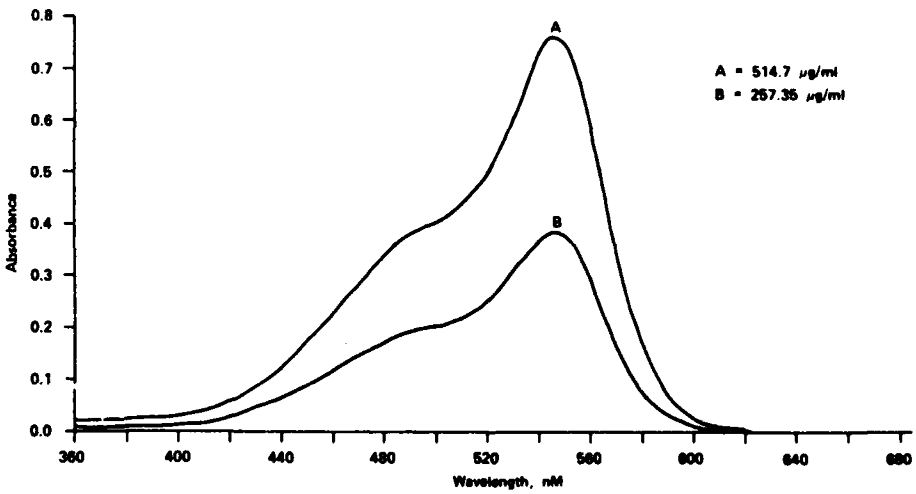


Figure 7. Spectral Characterization of Basic Fuchsin

Table 1. Minimal Detectable Analytical Sensitivity of PEG 200 Using 1% Dye Solutions

Dye Name	Absorb Maximum nm	Linear Regression Least-Squares Fitting	Minimal Detectable Analytical Sensitivity of PEG 200 Using 1% Dye Solutions
FD&C Blue #1	628	μg/ml = 0.7308 + 644.16 (absorb)	32.94 μg/ml
FD&C Yellow #6	480	μg/ml = -12.6622 + 2104.74 (absorb)	92.57 μg/ml
FD&C Green #3	624	μg/ml = 0.2891 + 644.106 (absorb)	33.49 μg/ml
FD&C Red #3	526	μg/ml = -3.6122 + 1117.885 (absorb)	52.28 μg/ml
Basic Fuchsin	546	μg/ml = 0.1465 + 625.7 (absorb)	31.4 μg/ml
Rhodamine B	554	μg/ml = -12.8974 + 2368.73 (absorb)	105.5 μg/ml

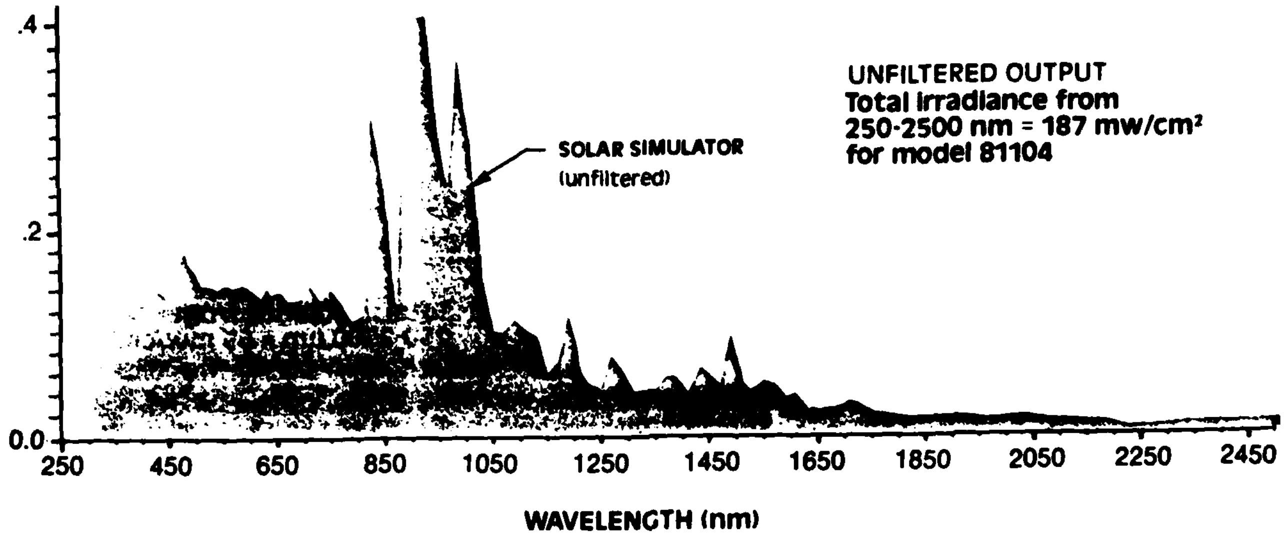


Figure 8. Unfiltered Irradiance Output from Oriel Solar Simulator

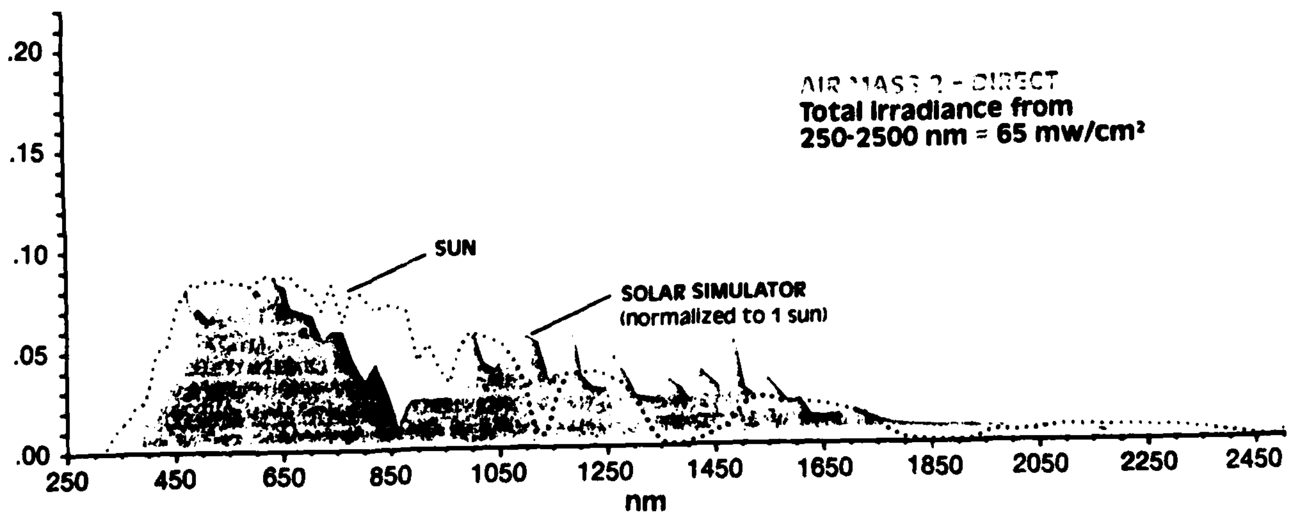


Figure 9. Irradiance Output from Solar Simulator Fitted with an Air Mass 2 Filter

Figures 10-15 show the photodecomposition curves for the dyes under study. Within the experimental error of the analysis performed, FD&C Yellow #6, FD&C Green #3, Basic Fuchsin, and FD&C Blue #1 show little, if any, decomposition. These samples were irradiated for 2 hr by the solar simulator, with an average irradiance of +79.95 mw/cm^2. The recoveries for these various dyes are shown in Table 2.

5. CONCLUSIONS

The studies indicate that FD&C Yellow #6, FD&C Green #3, Basic Fuchsin, and FD&C Blue #1 met the photostability requirements showing little decomposition while being exposed to solar radiation with an average irradiance of 79.95 mw/cm^2 or 68.79 cal • g/hr • cm^2. FD&C Red #3 and Rhodamine B proved to be unstable and decomposed rapidly. The half life of FD&C Red #3 is 73 min. During this time interval 83.92 cal • g/cm^2 impinged upon the sample area. During the half life of Rhodamine B (56 min), 63.97 cal • g/cm^2 impinged the sample area.

Basic Fuchsin, FD&C Green #3, and FD&C Blue #1 met the analytical sensitivity criteria only when employing a 2% dye solution or a 2-cm path cell. FD&C Yellow #6 and Rhodamine B would be satisfactory dye tracers at a 2% dye level and using a 5-cm path cell. A 1% dye level with a 5-cm path cell would be satisfactory for FD&C Red #3.

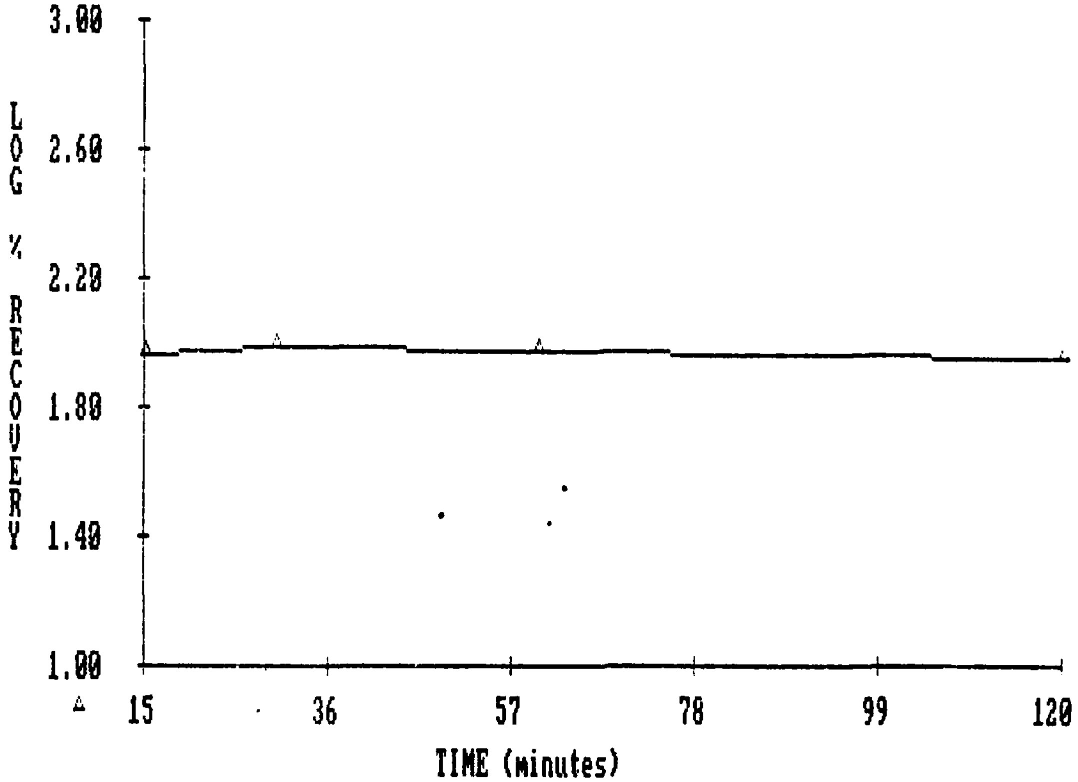


Figure 10. Photodecomposition of FD&C Yellow #6

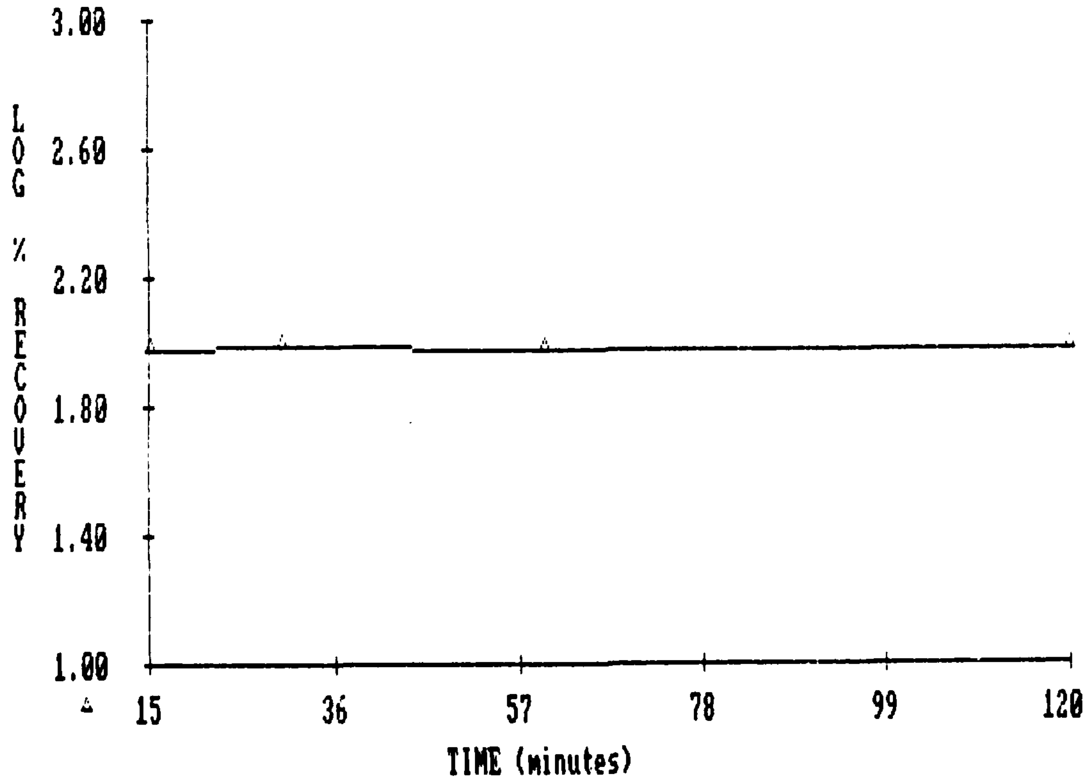


Figure 11. Photodecomposition of Basic Fuchsin

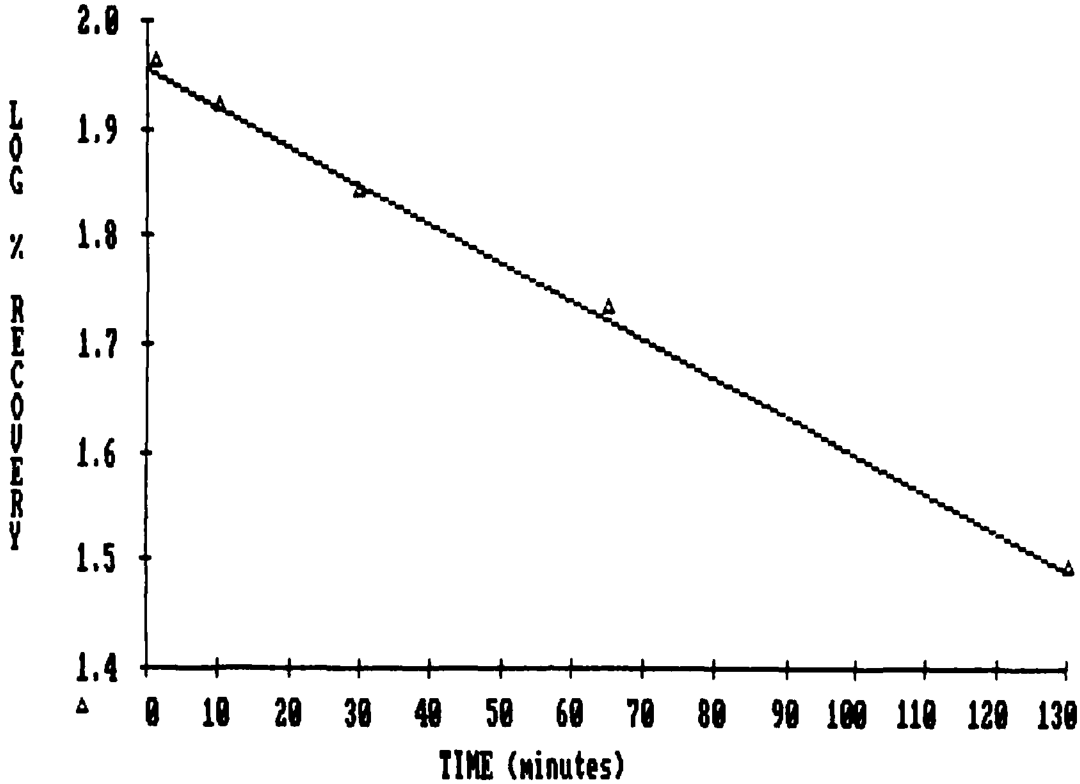


Figure 12. Photodecomposition of FD&C Red #3

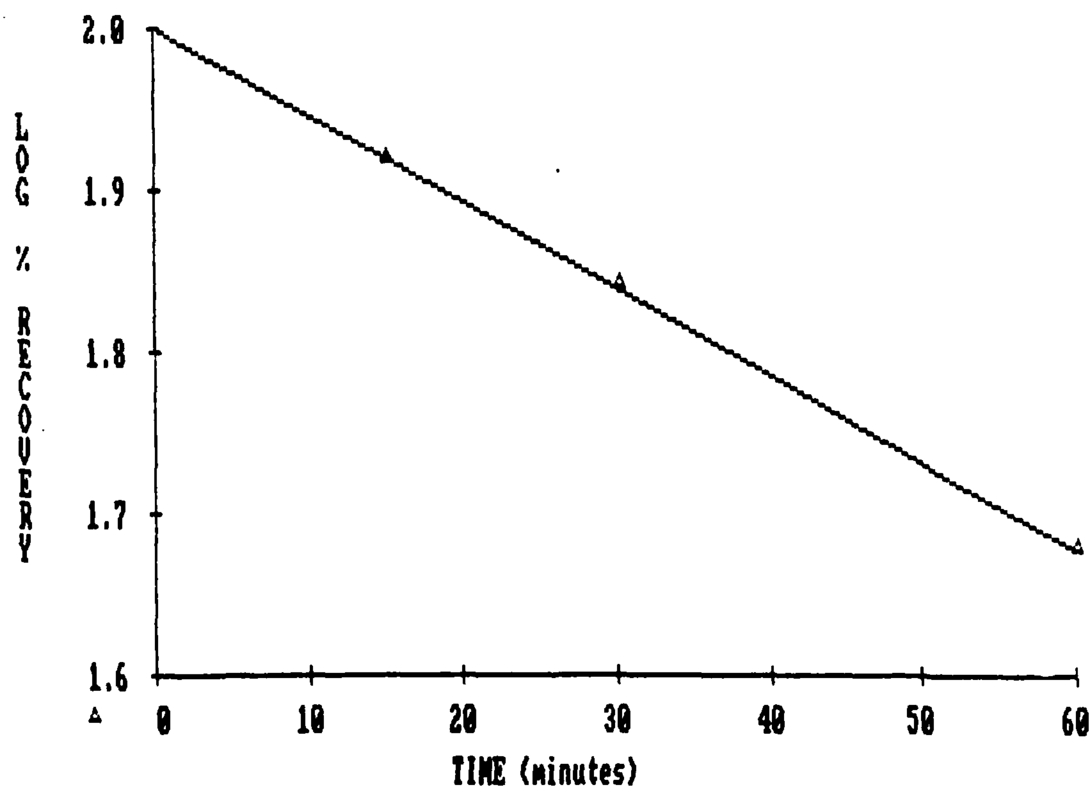


Figure 13. Photodecomposition of Rhodamine B

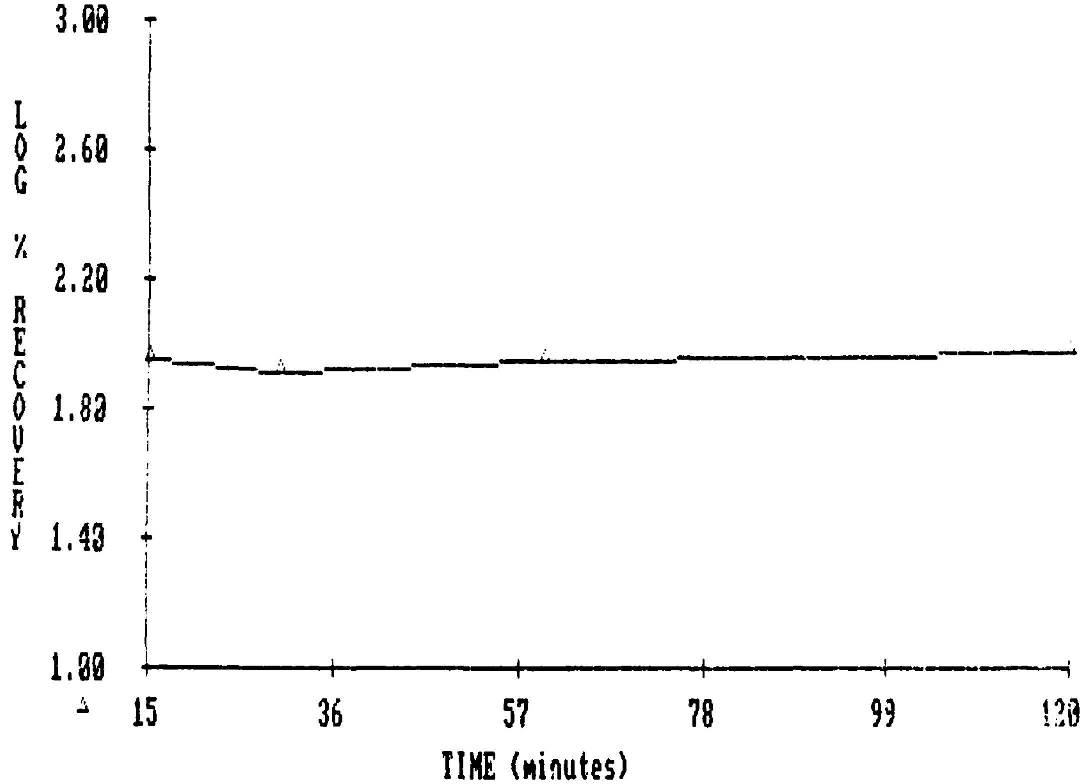


Figure 14. Photodecomposition of FD&C Green #3

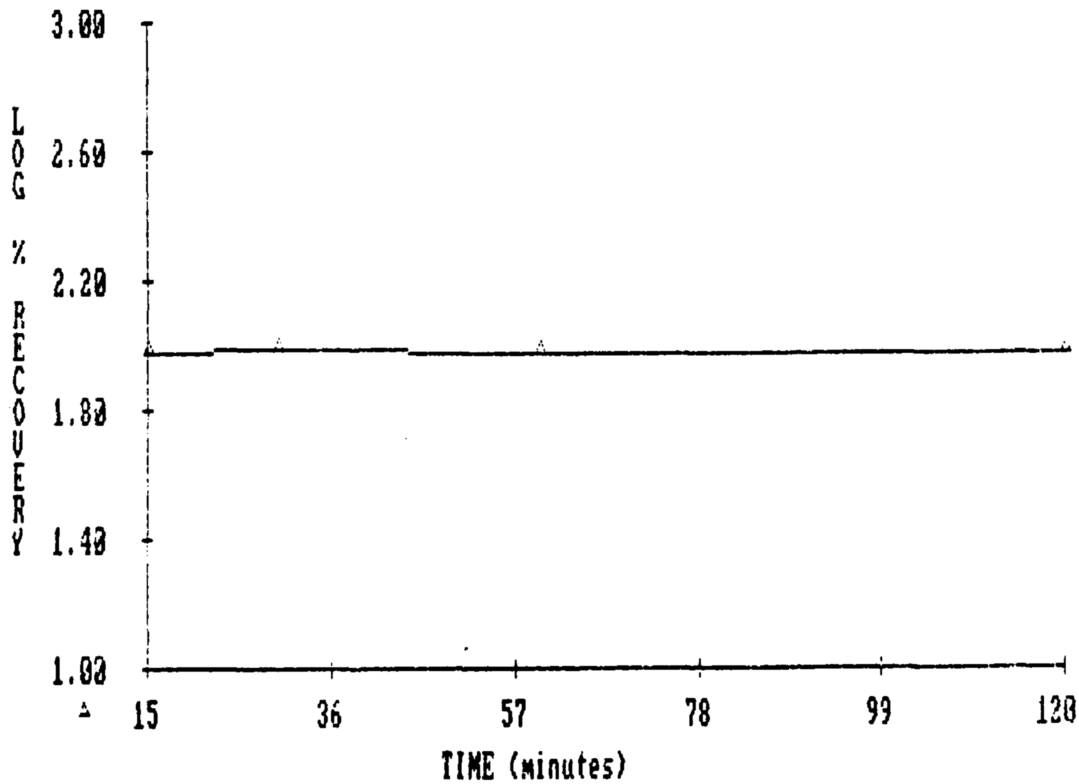


Figure 15. Photodecomposition of FD&C Blue #1

Table 2. Photodecomposition of Dye Tracers

BASIC FUCHSIN

Time (Min)	% Recovery	Log % Recovery	Irradiance (mw/cm^2)
15	97.15	1.98	79.34
30	99.8	1.99	78.37
60	96.35	1.98	77.4
120	96.3	1.98	78.05

FD&C BLUE #1

Time (min)	% Recovery	Log % Recovery	Irradiance (mw/cm^2)
15	96.0	1.98	76.11
30	97.4	1.99	76.11
60	95.6	1.98	77.4
120	95.3	1.98	78.05

FD&C YELLOW #6

Time (min)	% Recovery	Log % Recovery	Irradiance (mw/cm^2)
15	92.5	1.97	79.98
30	98.95	1.99	77.4
60	94.65	1.98	78.69
120	88.65	1.95	78.69

FD&C GREEN #3

Time (min)	% Recovery	Log % Recovery	Irradiance (mw/cm^2)
15	89.92	1.95	78.69
30	88.49	1.92	78.69
60	91.97	1.96	78.69
120	96.02	1.98	78.69

FD&C RED #3

Time (min)	% Recovery	Log % Recovery	Irradiance (mw/cm^2)
1	91.28	1.96	86.40
10	82.35	1.92	85.05
30	69.46	1.84	85.05
65	53.24	1.73	85.05
130	31.11	1.49	85.05

RHODAMINE B

Time (min)	% Recovery	Log % Recovery	Irradiance (mw/cm^2)
15	82.95	1.92	81.9
30	68.66	1.84	79.98
60	47.65	1.68	79.98

END
2-87
DTIC